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WESTINGHOUSE RESEARCH AND DEVELOPMENT CENTER PITTSBURGH
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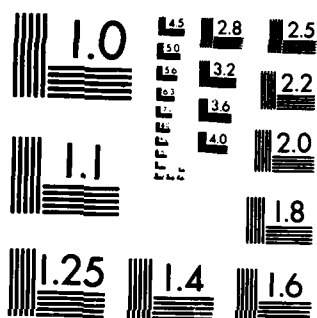
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Annual Report

AFOSR-TR- 84 - 0332

January 1, 1983 to December 31, 1983

**SUPERCONDUCTING ELECTRONIC FILM
STRUCTURES**

By

A. I. Braginski and J. R. Gavalier

Westinghouse Electric Corporation
Research and Development Center
Pittsburgh, Pennsylvania 15235

AFOSR Contract No. F49620-83-C-0035

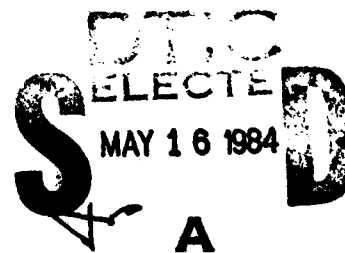
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1. Annual Report, Superconducting Electronic Film Structures

January 1, 1983 to December 31, 1983

AFOSR Contract No. F49620-83-C-0035

A. I. Braginski and J. R. Gavaler.

2. ABSTRACT

Single crystal NbN films were prepared on sapphire having a (2,-1,-1,3) surface orientation. Electron diffraction and Laue data show that the NbN and sapphire orientations are related, proving epitaxial growth. Al₅ structure V-Si and for the first time Al₅ Nb-Ge films were prepared reproducibly by a reactive sputtering process. These compounds were formed at temperatures as low as 500°C with critical temperatures above 12K. Niobium films were prepared at < 100°C with critical temperatures > 9K. Epitaxial quality Al₅ Nb-Ir single crystal substrates were prepared. A new magnetron sputtering system was implemented. Progress on the assembly and implementation of a MBE-type deposition and in situ analytical facility is reported.

3. OBJECTIVES

The objective of the Westinghouse-AFOSR program are:

1. Investigate the low-temperature synthesis of high-critical-temperature superconducting films.
2. Grow epitaxially single-crystal superconducting films and coherent layered structures.
3. Characterize the near-surface crystalline perfection of superconducting layers and their interfaces by in situ methods.
4. Study tunnelling into high-critical-temperature superconducting films and other electronic film properties.
5. Explore electric characteristics of layered film structures.

4. ACCOMPLISHMENTS

4.1 Preamble

This is a new research program initiated in January 1983. The research is aimed at understanding and improving superconducting and normal state properties of layered, epitaxial thin film structures incorporating high-critical-temperature superconductors. Anticipated results will form a material science base for future technology of high-operating temperature superconducting electronics. Successful completion of certain portions of this program requires a new type of deposition and in situ analytical facility hereafter termed as the Superlattice Facility (SF). This facility was delivered by Riber S. A. of France in the latter part of 1983. In this first year, the experimental work was performed in areas of the program for which the availability of the SF was not essential. Accomplishments in these areas and the present status of the new facility are detailed below:

4.2 Low-Temperature Synthesis of High- T_c Films

The investigation of possible means for synthesizing high- T_c superconducting films at low temperature ($\leq 500^\circ\text{C}$) was centered in two areas:

1. The reactive sputtering of V-Si and Nb-Ge films.
2. The magnetron sputtering of niobium films.

4.2.1 Reactive Sputtering of V-Si and Nb-Ge Films

Previous experience with reactive sputtering indicated that, in certain cases, compound formation can occur at a lower temperature with this technique compared to standard sputtering methods. This probably is due to the increased mobility and reactivity of atomic species introduced

in the form of a reactive gas. A series of deposition experiments have been completed in which V-Si and Nb-Ge films were deposited by reactively dc diode sputtering vanadium in an argon-SiH₄ mixture, and niobium in an argon-GeH₄ mixture. In both cases the deposition temperatures were varied from 950°C down to 350°C. By locating the reactive gas inlet tube near the end of a substrate holder supporting fifteen sapphire substrates, films were deposited in each experiment which had a wide range of V/Si (or Nb/Ge) ratios dependent on their distance from the inlet tube. This arrangement thus amounted to the "phase spread configuration" previously achieved by using elemental split targets. The chemical, structural, and electrical properties of these films were then determined.

Considering the V-Si results first, Al5 structure V₃Si was obtained at deposition temperatures (T_d) from 950°C down to 450°C. The V₃Si films sputtered between 950° and 650°C all had critical temperatures of ≥ 16 K. Below $T_d = 650^\circ\text{C}$ however T_c began to drop, and at $\leq 400^\circ\text{C}$ none of the films were superconducting. At $T_d = 500^\circ\text{C}$ (which is the cut-off temperature for "low-temperature" synthesis as defined for this program) the T_c 's obtained were as high as ~ 12 to 13K. Similarly encouraging results were obtained in the Nb-Ge growth experiments in that near-optimum T_c 's of ~ 21 K for Nb₃Ge were obtained in films deposited between ~ 950 and 650°C. T_c 's again dropped sharply below this temperature. However, at $T_d \sim 500$ K the critical temperature of the Nb₃Ge films were still above 12K. It is worthy of note here that these Nb-Ge experiments although not entirely successful at low substrate temperatures, were the first to reproducibly deposit high- T_c Nb₃Ge films by reactive sputtering. Previous results indicated that the Nb-Ge Al5 phase could be formed only non-reproducibly. This was attributed to the gettering of oxygen by GeH₄ and to the low background impurity level ($\sim 10^{-9}$ Torr) of the sputtering system in which these experiments were performed. It was theorized that some small level of oxygen is required to stabilize Nb₃Ge. In the present experiments the background pressure was $\sim 10^{-6}$ Torr which apparently provided sufficient oxygen to permit the stabilization of the Al5 phase.

Chemical analyses of the sputtered films showed that the V/Si and Nb/Ge ratios were not influenced by the substrate temperature down to 400°C, indicating that the decomposition of both GeH_4 and SiH_4 was independent of substrate temperature in the temperature range studied. The observed dependence of T_c upon the substrate temperature was similar to that previously found in the reactive sputtering of NbN films. In fact if the T_c data on Nb_3Ge and V_3Si films and the previous NbN data are normalized with respect to maximum T_c and plotted versus deposition temperature all of the $T_c/T_{c\text{max}}$ versus T_d points fall very nearly on a single curve. This result suggests that the degradation of T_c with substrate temperature in the V-Si and Nb-Ge films may be associated with the dc diode sputtering process, since it is known that when using magnetron sputtering, NbN films having close to optimum T_c 's (~ 15K) can be prepared on room temperature substrates. To study this possibility Nb_3Ge and V_3Si will be reactively sputtered in a magnetron system.

4.2.2 Magnetron Sputtering

As mentioned, it is known that magnetron sputtering is an effective tool for depositing certain superconductors at low temperatures without severely degrading their properties. This ability is due to the magnetic field deflecting the plasma away from the substrate area and thus minimizing damage to the depositing film. For this and other reasons it was deemed advisable to have a magnetron sputtering capability available for this program. A magnetron sputtering system has therefore been assembled (at no cost to AFOSR) and is now operational. A brief description of this system is given in Section 4.7 of this report. Initial deposition experiments have produced niobium films deposited at $T_d \sim 100^\circ\text{C}$ which have T_c 's of $> 9\text{K}$. This is approximately 250°C lower than the minimum temperature required to achieve 9K films when using the dc diode sputtering system used in the V-Si and Nb-Ge experiments. To increase the usefulness of the magnetron system it has been designed to be connected to the new UHV Superlattice Facility. This will then allow the in situ surface analyses of magnetron sputtered films as well as the ion beam and thermal treatment of the film substrates. Because it was

thought not to be desirable to introduce SiH_4 or GeH_4 gases into the new SF at this time, a second small magnetron sputtering facility is being constructed (also at no cost to AFOSR). This smaller facility will be exclusively used for the preparation of V_3Si and Nb_3Ge films by reactive sputtering. If results warrant, these experiments may ultimately be transferred to the SF.

4.3 Epitaxial Growth of Single Crystal Films and Coherent Layered Structures

4.3.1 Single Crystal NbN (B1) Films

As discussed in the Final Report of the Westinghouse-AFOSR program on "Ultrafine-Grained Superconductors," Contract No. F49620-78-C-0031, B1 structure NbN films can be prepared by dc diode sputtering amorphous Nb-N at low temperatures and then annealing the amorphous films at 600°C . When prepared under these conditions NbN films on sapphire substrates typically contain equiaxed grains with an average grain size of $\sim 275 \text{ \AA}$. An indication of the importance of the substrate material was obtained from observing films on niobium substrates. Although sputtered and annealed under the same conditions as those on sapphire, these films showed a columnar microstructure with the average column diameter being $> 1000 \text{ \AA}$. Some additional amorphous-crystallized NbN films deposited on sapphire substrates of various surface orientations were then studied by transmission electron microscopy. Most of these again showed equiaxed ultrafine grains similar to those observed before. However, two of these films were found to be single crystalline. One of the prime difficulties in obtaining single crystal film growth during any film deposition process is that the arrival of energetic particles at the substrate surface tends to disrupt the crystallization process. This difficulty seems to have been circumvented in the present approach since the film is first deposited in an amorphous state and then crystallization is apparently made to occur by annealing at an appropriate temperature. To confirm that epitaxial growth had occurred in these films, RHEED, TEM electron diffraction and Laue data were obtained on several sapphire substrates and their NbN overlayers in

both single crystal and polycrystalline films. Analysis of these data provided convincing evidence that in the case of the single crystal films the orientation of the NbN is indeed related to the orientation of the sapphire, thus proving epitaxial growth. The surface orientation of the sapphire was $\sim (2\bar{1}\bar{1}3)$. The sapphire in case of the polycrystalline films did not have this orientation.

With the existence of epitaxial growth having been confirmed there are now these questions to be answered:

1. How reproducible is this epitaxial growth method?
2. Does the nucleation of the NbN at the sapphire surface occur during the deposition step or during the subsequent annealing? In other words, is the as-deposited film amorphous indicating solid-state epitaxy, or is it microcrystalline indicating vapor-phase epitaxy?
3. Is more than one sapphire orientation conducive to epitaxial growth?
4. Are there other substrate materials which might be as good or better than sapphire?

These questions will be addressed during the next year of this program. The ability to grow single crystal NbN films could have important implications for a successful development of high-operating-temperature Josephson tunnel junctions.

4.3.2 Single Crystal Nb₃Ge (A15) Films

The epitaxial growth of A15 structure films is to be first investigated for the specific case of Nb₃Ge on single crystal Nb₃Ir substrates. This pair of A15 compounds has a close lattice parameter match, and observations interpreted as characteristic of "polycrystalline epitaxy" of Nb₃Ge on polycrystalline Nb₃Ir have been reported. Single crystals of Nb₃Ir were grown by pulling from a levitated melt and zone refining. This work was done through the courtesy of Dr. Eric Walker at

the University of Genève, Switzerland (at no cost to the program). The iridium metal was supplied by Westinghouse. To date two single crystal rods 6 mm in diameter were fabricated and are now being investigated at Westinghouse. Laue X-diffraction patterns indicated that the Nb_3Ir rods are single crystals with (100) major axis. Work on substrate fabrication by slicing, and epitaxial polishing is almost completed. Investigation of the quality of the surface treatment by RHEED is about to begin in the SF.

4.4 Characterization of Superconducting Layers and Their Interfaces by In Situ Methods

There were no results in this area of the program. Progress here depends on the implementation of the SF which is designed for in situ analyses.

4.5 Studies on Tunnelling in High- T_c Films and on Other Electronic Film Properties

Initial work in this area has involved V_3Si films made by dc reactive sputtering. One of the prime difficulties in obtaining good tunnelling data on V_3Si and other high- T_c superconductors is their extremely small coherence lengths, usually of the order of 50 Å. This means that any slight degradation of the superconductor surface during the fabrication of the tunnel junction will effect the accuracy of the data. This degradation can result from surface oxidation during the time between the deposition of the superconductor and the barrier layer. It can also occur from damage inflicted on the surface during the deposition of the barrier. Additionally, if the barrier layer is deposited by evaporation or sputtering, the coverage can be very non-uniform due to surface shadowing, unless the surface is extremely flat and smooth. For this program a barrier formation method is being investigated which could minimize all of these problems. After the above-mentioned high- T_c V_3Si films were reactively sputtered in an argon- SiH_4 atmosphere, the substrate temperature was lowered from 850 to 400°C. Sufficient SiH_4 (determined empirically) was then introduced into the system to produce a decomposition of SiH_4 into silicon at a rate of ~ 3 Å/min. The silicon layers were then

oxidized in air for 24 hours to produce the desired SiO_2 barrier layer. Analysis by XPS of a 40 Å SiO_2 barrier prepared by this technique showed that there was no oxidation of vanadium indicating complete coverage of the V_3Si . Further electrical and chemical characterization of these junctions are in progress.

4.6 Electric Characteristics of Layered Film Structures

No work on the preparation of layered film structures was done during this period.

4.7 Other Topics

Since the successful completion of a significant portion of the present research program is tied to the implementation of new deposition and analytical facilities a brief summary of the status of these facilities is given.

4.7.1 Magnetron Sputtering System I

The ultra-high vacuum sputtering chamber containing the magnetron sputtering guns has an oil-free pumping system consisting of an ion pump and titanium sublimation pump used to achieve a base pressure of 2×10^{-9} Torr. A cryopump is used to remove the argon sputtering gas. The cylindrical chamber has two six-inch flanges 90° apart on which are mounted U. S. Gun I sputtering heads. A third port on the same level will be used for a transfer rod which will connect to a small load-lock chamber and which can also connect to the SF. The sample holder assembly rotates to face either a magnetron gun or the transfer rod. It contains one heated stage capable of heating substrates to 950°C , one unheated stage, and a vibrating crystal thickness monitor. The temperature of the unheated samples floats to 100 to 150°C during deposition. The design of this system is such that it can (and soon will) be connected to the SF.

4.7.2 Magnetron Sputtering System II

As detailed in Section 4.2.1, the reactive sputtering of V_3Si and Nb_3Ge films requires the use of SiH_4 or GeH_4 gases and a background

impurity level of the order 10^{-6} Torr. Since the introduction of this type of contamination into the new UHV systems is deemed inadvisable at times, a second much simpler magnetron sputtering system is being constructed (at no cost to AFOSR). The system will have a single U. S. Gun I sputtering head, a high-temperature substrate heater, and mixing chamber for preparing the desired argon-GeH₄ or argon-SiH₄ mixture. This system will use diffusion pumping. The background pressure will be $\sim 10^{-6}$ Torr.

4.7.3 UHV Superlattice Facility

This facility which was described in detail in the Westinghouse Proposal No. 82M400 was delivered in October 1983. The installation by technical personnel of Ribier and Instruments SA was about 90% complete at year end with minor modifications to some deposition chamber hardware still being required before completion of the period of acceptance testing by Westinghouse. Standard system components, such as pumps, bakeout apparatus, transfer mechanisms, manipulators, heaters, effusion cells, etc. are performing very well, as Ribier continues to hold to their very high standards of component manufacture. The stringent vacuum attainment specifications were easily met early in the system installation.

The surface analysis package is operational (with the exception of integration with the DEC PDP11/23 computer and software) and will be in use even before acceptance testing is completed, initially for substrate characterization for epitaxial deposition work (Section 4.3.2).

The deposition part of the system will require the most effort to bring to a fully satisfactory state of operation, representing as it does the first effort by a UHV equipment manufacturer to produce a large, dual, rate-controlled refractory metal deposition system analogous to an MBE (molecular beam epitaxy) system. Westinghouse and ISA will continue working jointly, even after system acceptance, to improve the flux monitoring system so that the best possible deposition rate control can be achieved.

5. PUBLICATIONS

1. "Properties of NbN Films Crystallized from the Amorphous State,"^{*}
J. R. Cavalier, J. Gregg, R. Wilmer, and J. W. Ekin, IEEE Trans. on
Magnetics MAG-19, 418, 1983.
2. "The Upper Critical Field of NbN II,"^{*} M. Ashkin, J. R. Cavalier, J. Gregg,
and M. Decroux, Accepted for publication in the J. Appl. Physics.
3. "Epitaxial Growth of Superconducting Bl Structure NbN on Sapphire,"
J. R. Cavalier, J. Gregg, and J. Schreurs, Abstract to appear in Bull.
Am. Phys. Soc., March 1984, paper in preparation.
4. "Low Temperature Synthesis of V₃Si and Nb₃Ge by Reactive Sputtering,"
J. R. Cavalier, in preparation.
5. "Surface Acoustic Wave Evidence of a Kosterlitz-Thouless Transition
in a High Resistive NbN Film," A. Schenstrom, M. Levy, H. P.
Fredricksen, and J. R. Cavalier, Submitted to Phys. Rev. Letts.
6. "Superconducting Energy Gap Anomalies in NbN Films," H. P.
Fredricksen, M. Levy, M. Tachiki, M. Ashkin, and J. R. Cavalier, Sub-
mitted to Sol. State Comm.
7. "Pulsed Electron Beam Annealing of Al₅ Superconductors,"^{*} A. I.
Braginski, J. Gregg, M. A. Janocko, and O. Meyer, submitted to J.
Appl. Physics.

^{*}All or portions of these papers were prepared during the previous con-
tract period.

6. PERSONNEL

M. Ashkin

A. I. Braginski

J. R. Cavaler

J. Gregg

M. A. Janocko

J. Schreurs

J. Talvacchio

} Principal Co-Investigators

7. COUPLING ACTIVITIES

(Based in part on the preceding AFOSR program, Contract No. F49620-78-C-0031.)

1. "Potential of B1 Superconductors for High-Field Fusion Applications: Some New Results," A. I. Braginski, M. Ashkin, J. R. Gavaler, and J. Gregg, invited talk at the US-Japan Workshop on Superconducting Materials for Fusion, San Diego, May 23-27, 1983.
2. Participation in the NATO Advanced Study Institute on "Percolation, Localization and Superconductivity," A. I. Braginski, Les Arcs, France, June 19-July 1, 1983.
3. Participation in the CEC/ICMC (International Cryogenic Materials Conference), A. I. Braginski, Colorado Springs, August 15-19, 1983.
4. "Thin Film Materials," A. I. Braginski, invited presentation at the Workshop on Problems in Superconductivity, Copper Mountain, Colorado, August 21-23, 1983.

8. PATENTS AND INVENTIONS

1. "Method and Apparatus Utilizing Crystalline Compound Superconducting Elements Having Extended Strain Operating Range Capabilities Without Critical Current Degradation," J. W. Ekin, J. R. Gavaler, and A. I. Braginski, U. S. Patent approved, not issued yet.